

Infrared and Raman spectra of $\text{Si}(\text{C}\equiv\text{CH})_4$ and $\text{Ge}(\text{C}\equiv\text{CH})_4$, and the infrared spectrum of $\text{Sn}(\text{C}\equiv\text{CH})_4$

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Abstract—Infrared spectra of $\text{Si}(\text{C}\equiv\text{CH})_4$, $\text{Ge}(\text{C}\equiv\text{CH})_4$, and $\text{Sn}(\text{C}\equiv\text{CH})_4$ have been measured from 33 to 4000 cm^{-1} for the vapor and for solutions in several solvents. Raman spectra with polarizations were obtained for solutions of the first two compounds only. T_d symmetry was assumed and was completely satisfactory. Most of the spectroscopically-active fundamentals of the silicon and germanium compounds could be assigned with little difficulty.

1. INTRODUCTION

OUR two laboratories have been working for some time with acetylenic derivatives of several of the metalloid elements. At Mellon Institute the vibrational spectra of $\text{P}(\text{C}\equiv\text{CH})_3$, $\text{As}(\text{C}\equiv\text{CH})_3$, and $\text{Sb}(\text{C}\equiv\text{CH})_3$ have recently been studied [1]. At the Natick Laboratories the emphasis has been on the preparation and properties of various ethynyl compounds. Of special interest to us were the studies on $\text{Si}(\text{C}\equiv\text{CH})_4$ and $\text{Ge}(\text{C}\equiv\text{CH})_4$ by DAVIDSOHN and HENRY [2], and on $\text{Sn}(\text{C}\equiv\text{CH})_4$ by FINDEISS [3]. This paper results from a cooperative effort to study the infrared and Raman spectra of these last three compounds: tetraethynylsilane, -germane, and -stannane.

There is almost no prior work on the spectroscopy of these compounds, and there is none whatever on their structure. SHOSTAKOVSKII *et al.* [4], in a paper dealing with band intensities, presented the infrared spectrum of $\text{Si}(\text{C}\equiv\text{CH})_4$ in CCl_4 solution in the form of a small figure. Numerical frequencies were given for only two bands: the $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ stretches. There was no comment on the preparation or properties of the compound. The same two bands were also mentioned briefly in another paper on intensities [5]. DAVIDSOHN and HENRY [2] gave five infrared bands for both the Si and Ge compounds in their paper dealing

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[1] F. A. MILLER and D. H. LEMMON, *Spectrochim. Acta* **23A**, 1099 (1967).

[2] W. DAVIDSOHN and M. C. HENRY, *J. Organometal. Chem.* **5**, 29 (1966).

[3] W. FINDEISS, unpublished results, U.S. Army Natick Laboratories, Natick, Mass.

[4] M. F. SHOSTAKOVSKII, N. I. SHERGINA, E. I. BRODSKAYA, O. G. YAROSH and N. V. KOMAROV, *Dokl. Akad. Nauk SSSR* **158**, 1143 (1964); *Eng. Transl.* p. 1085; *Chem. Abs.* **62**, 6012h (1965).

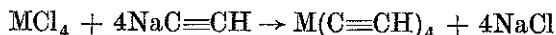
[5] E. A. GASTILOVICH, D. N. SHIGORIN, N. V. KOMAROV and O. G. YAROSH, *Opt. i Spektroskopiya* **19**, 287 (1965); *Opt. Spectry (USSR)* **19**, 162 (1965).

with the syntheses. $\text{Sn}(\text{C}\equiv\text{CH})_4$ was first prepared by JENKNER [6], who reported three infrared bands at 690, 2050 and 3300 cm^{-1} .

Thus no real work has been done on the vibrational spectra of these compounds. Their novelty and presumably high symmetry make a study attractive.

2. SOURCES AND PROPERTIES OF THE COMPOUNDS

The samples were provided through the courtesy of Drs. Davidsohn, Henry and Findeiss of the Natick Laboratories, who synthesized them by the general reaction



The preparations were attended by several violent explosions.

All three compounds are colorless solids which sublime readily at room temperature under vacuum. The melting points are 88–89, 91–92 and 67° for the Si, Ge and Sn compound respectively. (It is odd that the melting point is lowest for the Sn compound.) All three substances are potentially explosive and should be handled with great caution. Care was taken to avoid heat, shock and friction and to work with small quantities of the compounds. Even though we were very careful, we had a violent explosion of unknown origin while making a vacuum transfer of tetraethynyl tin. The compounds can be kept for an indefinite period if cool and dry, but they slowly darken on exposure to light.

The analogous $\text{Pb}(\text{C}\equiv\text{CH})_4$ has never been reported. Its synthesis is probably very dangerous, since compounds with only one $\text{Pb}-\text{C}\equiv\text{C}$ unit have exploded violently, and instability generally increases as the number of ethynyl substituents increases.

3. SPECTROSCOPIC PROCEDURES AND RESULTS

Raman spectra were obtained with a Cary Model 81 Raman spectrophotometer on solutions in carbon tetrachloride, cyclohexane and furan. The 7-mm diameter Raman tubes were used, and the spectral slit width was 10 cm^{-1} . Qualitative polarizations were obtained by the usual two-exposure method employing cylinders of Polaroid concentric with the Raman tube.

Infrared spectra were obtained from 33 to 4000 cm^{-1} using Beckman IR-11 and IR-12 spectrophotometers. The resolution was $1\text{--}2\text{ cm}^{-1}$. For the vapor phase measurements, path lengths ranged from 10 cm to 8.2 m. Spectra were also obtained for carbon tetrachloride, cyclohexane and benzene solutions.

The data are given in Tables 1–3 and in Fig. 1. Raman frequencies are believed to be accurate to $\pm 2\text{ cm}^{-1}$, infrared ones to $\pm 1\text{ cm}^{-1}$.

4. ASSIGNMENTS

4.1 Choice of symmetry

The molecules are expected to belong to the tetrahedral point group T_d . This symmetry was therefore assumed initially. It proved to be completely satisfactory, and we feel that there is no need to even consider any other symmetry.

[6] H. JENKNER, German Patent 1,152,106 (August 1963); *Chem. Abs.* **60**, 552b (1964).

Table 1. $\text{Si}(\text{C}\equiv\text{CH})_4$: Raman and infrared spectra (in cm^{-1})

CCl_4	Raman (solution)		Polzn.	Infrared				Assignment
	Cyclo-hexane	Rel. inten.		CCl_4	Cyclo-hexane	Gas	Inten.	
105.5	102.5	65	dp			97.5		ν_8
				115		103	m	ν_{14}
						106.5	sh	
357	359	9	dp			387.5	sh	ν_5
				392	392*	392.5	s	ν_{13}
						396	sh	
						432.5	vw	$534 - 103 = 431$ (a)
						470	vw	?
						491.5	vw	$392.5 + 103 = 495.5$
534	530.5	5	p					ν_3
				580	580*	576	w	?
				612	612*	606	w	$708 - 103 = 605$ (a)
					679	687	m	ν_{12}
695	690.5	6	dp					ν_4
					707	708	vs	ν_{11}
					718		vw	?
					724	729	w	?
					738	745	w	$357 + 392 = 749$
						1353		
				1368	1362	1360	m	$2 \times 687 = 1374$
						1367		
				2009			vw	?
				2028			vw	$3 \times 679 = 2037?$
2053	2053.5	100	p					ν_2
				2055	2056	2062	s	ν_{10}
						3291	vw, sh	?
						3296	w	?
3298	3299	9	p					ν_1
						3309		
				3297	3287	3315	s	ν_9
						3321		
				3970	3968	3980	w	$3298 + 687 = 3985$

w, m, s = weak, medium, strong; v = very; sh = shoulder; p, dp = polarized, depolarized.

* In benzene.

(a) Corresponding sum tone not observed. See discussion.

Table 4 lists the normal vibrations and our assignments for the three molecules. The assignments are also included in Tables 1-3.

In the following discussion we shall use the gas frequencies if available, and as second choice frequencies in CCl_4 solution.

4.2 $\text{Si}(\text{C}\equiv\text{CH})_4$

4.2.1 *Species a_1* . Raman polarizations make the choice of 3298, 2053 and 534 cm^{-1} for ν_1 , ν_2 and ν_3 completely certain.

4.2.2 *Species e* . These three fundamentals are only Raman-active and are depolarized. The three lines at 695, 357 and 105.5 cm^{-1} are obvious choices, and we assign them to ν_4 , ν_5 and ν_6 respectively.

4.2.3 *Species f_2* . These six fundamentals are both Raman and infrared active. The $\text{C}\equiv\text{H}$ stretch, ν_9 , is clearly 3315 cm^{-1} in the vapor. In CCl_4 solution the infrared frequency is 3297 cm^{-1} , which is only 1 cm^{-1} different from the polarized Raman line already assigned to ν_1 . There are two reasons for believing that they do arise from different normal vibrations: (a) In cyclohexane solution the Raman

Table 2. $\text{Ge}(\text{C}\equiv\text{CH})_4$: Raman and infrared spectra (in cm^{-1})

Raman (solution)				Infrared				Assignment
CCl_4	Cyclo-hexane	Rel. inten.	Polzn.	CCl_4	Cyclo-hexane	Gas	Inten.	
98	98	60	dp	102		87 } 90.5 } 93.5 }	w	ν_{14} (and ν_6 ?)
						316	vw	?
346†	346	8	dp	354*	352	355.5	s	ν_5
						436	vw	ν_{13}
								$523 - 90.5 = 432.5$ (a)
507	508	16	p			523	m	ν_3
				525	522.5	580	m	ν_{12}
				582	581	668	w	?
						667	w	$580 + 90.5 = 670.5$
689	686	12	dp	688	684	683	vs	ν_{11}
						1344 }		
				1356		1350 }	s	$2 \times 683 = 1366$
						1356 }		
				2012			vw	?
				2030			vw	$3 \times 688 = 2064$?
				2055	2057	2062	m	ν_{10}
2057	2059	100	p					ν_2
3298	3301.5	12	p					ν_1
						3291	vw, sh	?
						3296	w	?
						3310		
				3299	3299	3315.5 }	s	ν_9
						3321 }		
				3967	3964	3979	vw	$3298 + 683 = 3981$

* In benzene.

† In furan.

(a) Corresponding sum tone not observed. See discussion for $\text{Si}(\text{C}\equiv\text{CH})_4$.

Abbreviations as in Table 1.

Table 3. $\text{Sn}(\text{C}\equiv\text{CH})_4$: infrared spectrum (in cm^{-1})

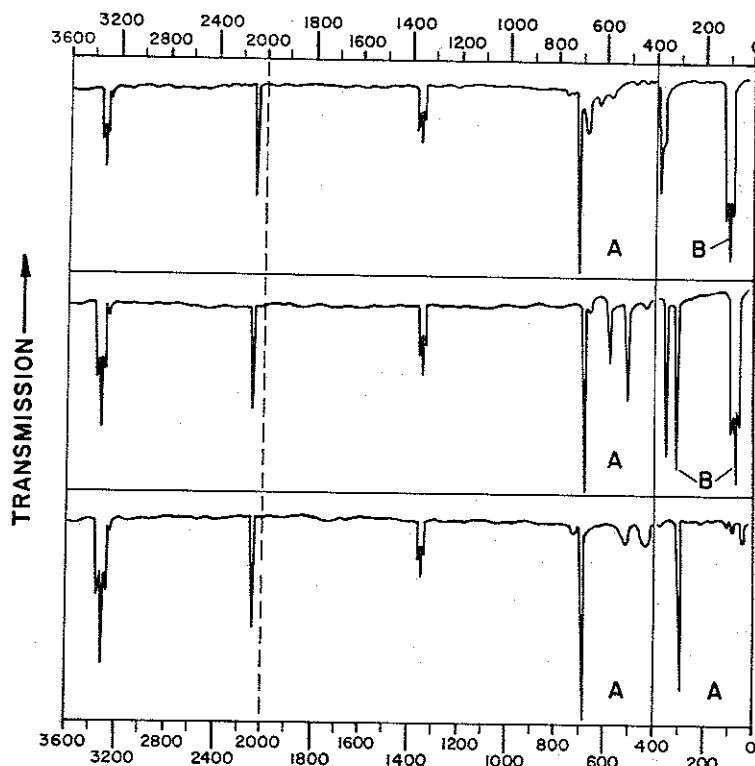
CCl_4	Benzene	Gas	Intensity	Assignment
		45	w-m Real?	ν_{14} ?
		97	w Real?	ν_{14} ?
		116	vw Real?	?
		217	vw Real?	?
289	290	290*	s	ν_{13}
		387*	w	$290 + 97 = 387$?
448 } *	450 } *	447 } *	w-m	ν_{12} ?
505 }	506 }	504 }	w-m	ν_{12} ?
688		686	vs	ν_{11}
733		730	w	$686 + 45 = 731$?
		1347 }		
1357	1356	1352 }	m	$2 \times 686 = 1372$
		1357 }		
2037	2034	2043	m	ν_{10}
		3286	vw-sh	?
		3291	w	?
3274 }	3273 }	3306 }		
3293 }	3280 }	3311 }	s	ν_9
		3316 }		
	3958	3975	vw	?

* In the solid at 100°K, these bands are 282 (s), 376 (w) and 470 (m).

Table 4. Fundamental vibrations of $\text{Si}(\text{C}\equiv\text{CH})_4$, $\text{Ge}(\text{C}\equiv\text{CH})_4$ and $\text{Sn}(\text{C}\equiv\text{CH})_4$ (T_d symmetry)

T_d Species	Activity	No.	Schematic description	$\text{Si}(\text{C}\equiv\text{CH})_4$	Assignments $\text{Ge}(\text{C}\equiv\text{CH})_4$	$\text{Sn}(\text{C}\equiv\text{CH})_4$
a_1	R (p), —	1	C—H stretch	3298	3298	
		2	C≡C stretch	2053	2057	
		3	M—C stretch	534	507	
e	R (dp), —	4	C≡C—H bend	695	?	
		5	M—C≡C bend	357	346	
		6	C—M—C deformation	105.5	98?	
f_1	—, —	7	C≡C—H bend	—	—	
		8	M—C≡C bend	—	—	
f_2	R (dp), IR	9	C—H stretch	3315	3315.5	3311
		10	C≡C stretch	2062	2062	2043
		11	C≡C—H bend	687	683	686
		12	M—C stretch	708	523	504 or 447
		13	M—C≡C bend	392.5	355.5	290
		14	C—M—C deformation	103	90.5	97 or 45?

M = Si, Ge, or Sn.

Fig. 1. Infrared spectra of $\text{Si}(\text{C}\equiv\text{CH})_4$, upper $\text{Ge}(\text{C}\equiv\text{CH})_4$ and $\text{Sn}(\text{C}\equiv\text{CH})_4$ lower (A) 10 cm path, (B) 8.2 m path (all at equilibrium vapor pressure). Note change of scale at 2000 cm^{-1} .

value is 3299 cm^{-1} , whereas the infrared one is 3287 cm^{-1} . The difference is well outside of experimental error. (b) A polarized Raman line cannot be infrared-active for T_d symmetry. If T_d symmetry were abandoned, many serious obstacles would arise in making the assignments. It is much more reasonable to believe that this is a case of very near coincidence of two fundamentals. The $\equiv\text{C}-\text{H}$ groups are so far apart physically that they may well vibrate almost independently of one another.

For the $\text{C}\equiv\text{C}$ stretch ν_{10} the value is 2062 cm^{-1} in the vapor. In CCl_4 and C_6H_{12} solution the value is $2-2.5\text{ cm}^{-1}$ different from the polarized Raman line assigned to ν_2 . Again we believe that this is a case of accidental degeneracy. Coupling between the stretches of two $\text{C}\equiv\text{C}$ groups would have to take place through two single bonds and the relatively heavy central atom, and therefore may well be very weak.

We shall find similar accidental coincidences between the two $\equiv\text{C}-\text{H}$ stretches, and between the two $\text{C}\equiv\text{C}$ stretches, in the Ge and Sn compounds. They were also observed for $\text{P}(\text{C}\equiv\text{CH})_3$, $\text{As}(\text{C}\equiv\text{CH})_3$ and $\text{Sb}(\text{C}\equiv\text{CH})_3$ [1].

The next two f_2 fundamentals, ν_{11} and ν_{12} , are assigned to the very strong 708 and the much weaker 687 cm^{-1} band (Fig. 1). One is nominally a $\text{C}\equiv\text{C}-\text{H}$ bend and the other a $\text{Si}-\text{C}$ stretch. It is difficult to make a definite assignment for either band, and there is a possibility that they may be mixed. Two arguments point to 687 being a relatively pure bend. (1) 687 cm^{-1} is very close to the $\text{C}\equiv\text{C}-\text{H}$ bends in the Ge and Sn compounds (683 and 686 cm^{-1}), where the $\text{M}-\text{C}$ stretches are located outside of this region. (2) It is characteristic of the $\text{C}\equiv\text{C}-\text{H}$ bend that its overtone is unusually intense. This can be seen clearly in Fig. 1. The observed overtone seems to arise from 687 rather than from 708, as shown below:

	Calculated	Observed	Diff.
$\text{Si}(\text{C}\equiv\text{CH})_4$	$2 \times 708\text{ (vs)} = 1416$	1360	56
	$2 \times 687\text{ (m)} = 1374$	1360	14
$\text{Ge}(\text{C}\equiv\text{CH})_4$	$2 \times 683\text{ (vs)} = 1366$	1350	16
$\text{Sn}(\text{C}\equiv\text{CH})_4$	$2 \times 686\text{ (vs)} = 1372$	1352	20

However there is an argument in favor of 708. In the Ge and Sn compounds the $\text{C}\equiv\text{C}-\text{H}$ bend is the strongest band in the infrared spectrum. In the $\text{Si}(\text{C}\equiv\text{CH})_4$ spectrum, it is 708 whose intensity and general appearance matches that of the 683 and 686 cm^{-1} bands in the other two compounds, whereas 687 is an unimpressive band on the side of 708.

Thus, the situation is not clear, and probably there is considerable mixing of the modes. We have indicated this by brackets in Table 4.

The two remaining f_2 fundamentals, ν_{13} and ν_{14} , are reasonably assigned to 392.5 and 103 cm^{-1} respectively. The former is not observed in the Raman spectrum; this is also true for ν_{13} in the Ge compound.

4.2.4 Remaining bands. Explanations for the remaining bands are included in Table 1. With one exception only binary combinations were used, and all but 7 weak bands have been accounted for.

Two difference tones have been assigned (432.5 and 606 cm^{-1}) for which the corresponding sum tones were not observed. The 432.5 band was measured with an 8.2 m path, whereas the region of the corresponding sum tone (approximately 637 cm^{-1}) was examined with only a 10 cm path. Another explanation is required for the 606 band. Both the difference tones use 103 cm^{-1} as the lower state. Because 103 cm^{-1} is low and is triply degenerate, its Boltzmann population at 27°C is 1.8 times that of the ground state. Therefore, a difference tone starting from this level is expected to be more intense than the corresponding sum tone.

We could not find any evidence for the two totally-inactive f_1 fundamentals from the remaining bands.

4.3 $\text{Ge}(\text{C}\equiv\text{CH})_4$

4.3.1 Fundamentals. For the three a_1 modes, 3298 , 2057 and 507 cm^{-1} are the clear choices from Raman polarizations. For the three e modes there is only one obvious candidate: the Raman band at 346 cm^{-1} , which is best attributed to ν_5 . There is no evidence for the $\text{C}\equiv\text{C}-\text{H}$ bend ν_4 . It may be accidentally degenerate with the f_2 bend ν_{11} at 689 cm^{-1} . (In the Si compound they were only 11 or 17 cm^{-1} apart.) Also, of course, it may have been unobserved because of weakness. Similarly ν_6 may be very close to the f_2 deformation ν_{14} . Analogy with the Si compound suggests that the 98 cm^{-1} Raman line is ν_6 and the 102 cm^{-1} infrared band (CCl_4 value) is ν_{14} . However the two frequencies are so close together that they may both be due to ν_{14} .

Turning to species f_2 , 3315.5 and 2062 cm^{-1} are obviously $\sqrt{9}$ and $\sqrt{10}$. As for $\text{Si}(\text{C}\equiv\text{CH})_4$, in solution both infrared bands become essentially coincident with polarized Raman lines. The $\text{C}\equiv\text{C}-\text{H}$ bend is certainly 683 cm^{-1} , but the $\text{Ge}-\text{C}$ stretch ν_{12} offers a problem. It may be either 580 or 523 . We cannot explain either one as a binary combination, so we choose 523 because it is slightly more intense.

The band at 355.5 cm^{-1} is an obvious choice for ν_{13} . One might wonder whether this is not really due to the same vibration as the Raman frequency at 346 . We think not, because in cyclohexane solution the Raman and infrared frequencies differ by 6 cm^{-1} , which we believe is outside of experimental error. Finally ν_{14} is certainly 90.5 cm^{-1} .

4.3.2 Remaining bands. There are six bands for which there is no satisfactory explanation based on a binary combination. Since four fundamentals are still unassigned, this is not serious. The most important band to account for is 580 cm^{-1} (or 523 , if 580 is assigned to ν_{12}). We have been unable to do so. Since two of the unknown fundamentals, ν_6 and ν_8 , are well below 500 cm^{-1} , they may be involved in the explanation. It may be, too, that 523 and 580 are in Fermi resonance, although we have no specific combination to suggest.

4.4 $\text{Sn}(\text{C}\equiv\text{CH})_4$

Only the infrared results are reported for this compound because the sample was unfortunately lost by explosion before the Raman data were measured. The bands at 3311 , 2043 and 686 cm^{-1} are certainly ν_9 , ν_{10} and ν_{11} . The identification of ν_{12} , the $\text{Sn}-\text{C}$ stretch, poses a problem because there are two good candidates at 504 and 447 cm^{-1} , of about equal intensity. We cannot explain either as a

combination or overtone, but this may not be significant because the Raman data are missing. These bands may also be in Fermi resonance because in the solid at low temperature only a single band at 470 cm^{-1} was found. The 290 cm^{-1} band is clearly ν_{13} and ν_{14} may be either 97 or 45. However there is some doubt about the reality of the latter two, for in measuring the spectrum of the solid at 100°K we could find no bands below 250 cm^{-1} .

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